THE CLUSTERING OF O2 AND He TO Li(+)

Ballistic Research Laboratories

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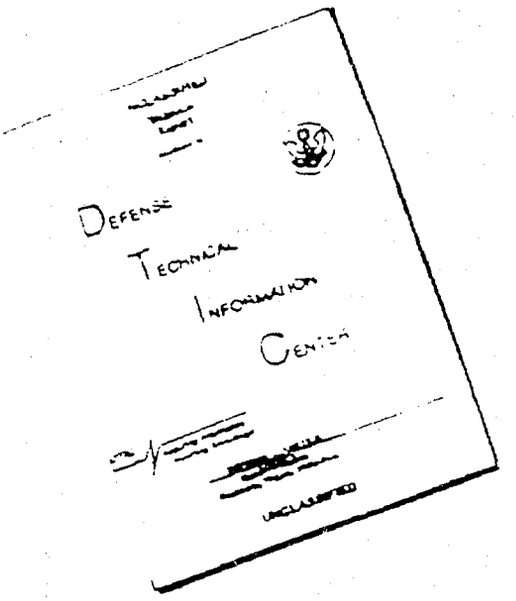

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THE CLUSTERING OF O_2 AND He TO Li^+

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USA BALLISTIC RESEARCH LABORATORIES
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SUMMARY

The clustering of oxygen and helium to positive lithium ions has been studied using a drift tube-mass spectrometer at 319K. For oxygen clustering, the rate coefficients for cluster ion formation and collisional dissociation were measured as a function of E/N. For clustering to helium, only an equilibrium constant was determined. The relative importance of the clustering of several atmospheric gases to positive lithium ions in the ionosphere is discussed.

INTRODUCTION

The performance of communications systems, radars, and other defense systems are predicted using phenomenology codes which employ simplified chemistry. Extensive chemical codes of the lower ionosphere are being developed in our laboratory to check the reliability of the simplified chemistry. The development of these large chemical codes requires both *in situ* measurements of ionic- and neutral-constituent densities in the lower ionosphere and laboratory measurements of relevant reaction rate coefficients. This report contains recent results of the BRL laboratory measurements program which determines these reaction rate coefficients.

RESULTS AND DISCUSSION

The clustering of O_2 to Li^+ has been studied using a drift tube-mass spectrometer at 319K. The gas pressure was varied between 66.7 and 200.0 N/m^2 (0.5 and 1.5 Torr) and the E/N (the ratio of the uniform electric field in the drift region to the neutral number density) between 1.2 and 2.4 x 10^{-20} $V\,m^2$. The only ions observed were Li^+ and $Li^+(O_2)$; therefore, we assume that the reactions:

$$Li^+ + 2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Li^+(O_2) + O_2$$

dominate the ion chemistry.

The apparatus and experimental technique have been described previously[1,2] in papers describing the clusters of Ar and N_2 to Li^+. Time-of-arrival spectra for Li^+ and $Li^+(O_2)$ were recorded for various pressure and E/N combinations within the ranges given above. These spectra were compared with spectra computed using the method of Gatland[3] for two interconverting ions. At a given E/N we sought the set of parameters which resulted in the best comparison of the experimental and theoretical spectra for both ions at three different pressures. Typical comparisons are shown in Figures 1 and 2.

The deduced rate coefficients are shown in Table I as a function of E/N. Note that the association-rate coefficients are essentially constant over the range of E/N studied, whereas the collisional-dissociation-rate coefficients increase with increasing E/N. The amounts by which these rate coefficients may be in error are estimated to be ±24% for the association-rate coefficients and ±22% for the collisional-dissociation-rate coefficients.

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[1] G. E. Keller, R. A. Beyer, and L. M. Colonna-Romano, Phys. Rev. A 8, 1446 (1973). Also available as BRL Report No. 1691, December 1973, AD #773668.

[2] I. R. Gatland, L. M. Colonna-Romano, and G. E. Keller, Phys. Rev. A 12, 1885 (1975). Also available as BRL Report No. 1858, February 1976, AD #A021522.

[3] I. R. Gatland, "Ion Swarm Analysis," Technical Report of the Georgia Institute of Technology, June 1972. See also I. R. Gatland, Case Studies in Atomic Physics 4, 369 (1974).

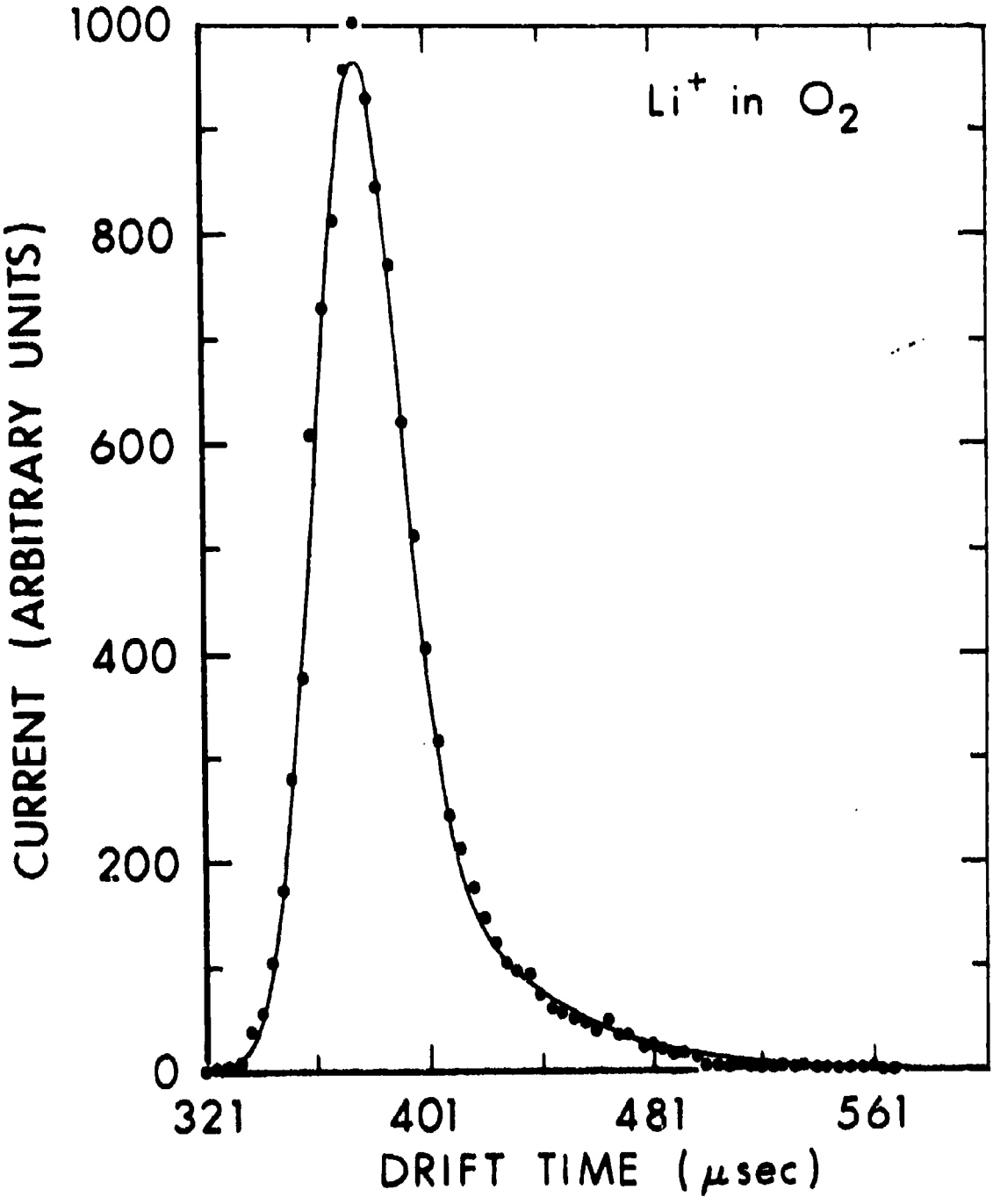

Figure 1. Comparison of experimental data with model calculations for Li^+. $E/N = 1.8 \times 10^{-16}$ V cm^2, p = 1.00 Torr, T = 319 K. The dots are measurements, and the smooth curves are the model calculations.

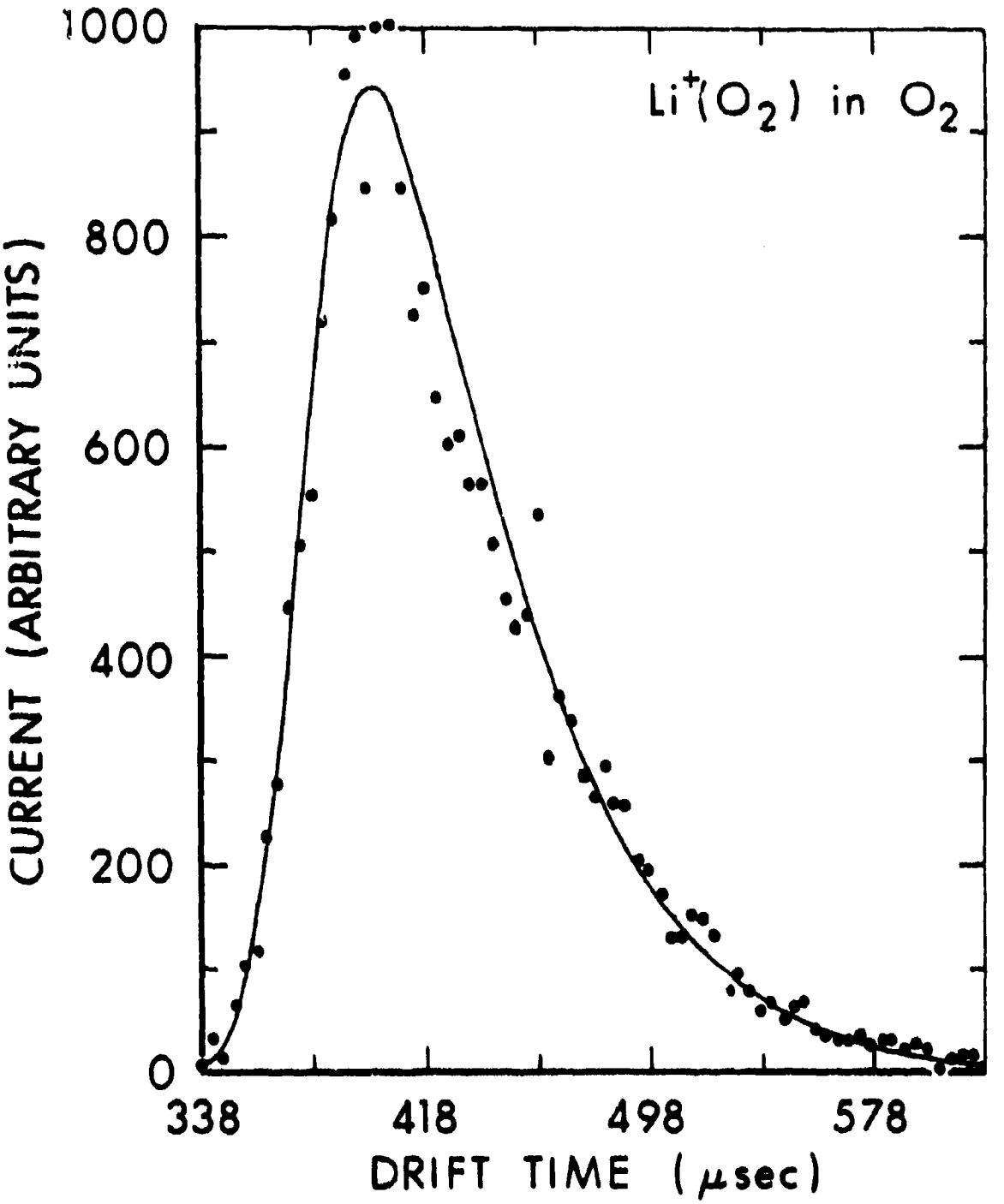

Figure 2. Comparison of experimental data with model calculations for $Li^+(O_2)$ under the same conditions as in Figure 1. The dots are measurements and the smooth curves are model calculations.

TABLE I. THE ASSOCIATION-RATE COEFFICIENTS AND THE COLLISIONAL-DISSOCIATION-RATE COEFFICIENTS FOR THE CLUSTERING OF O_2 TO Li^+.

E/N ($\times 10^{-20}$ V m^2)	k_1 ($\times 10^{-42}$ $m^6 sec^{-1}$)	k_{-1} ($\times 10^{-19}$ $m^3 sec^{-1}$)
1.2	1.08	3.5
1.5	1.10	4.0
1.8	1.10	4.2
2.1	1.08	4.6
2.4	1.09	4.9

The mobilities of the two ions were also deduced. The Li^+ arrival profiles have the expected skewed Gaussian shape plus a contribution at late times from ions which emerged from the tube but had spent some time as the slower cluster ions. We used the mean arrival time of the skewed Gaussian portion of these profiles to determine the mobility of Li^+ in O_2. The reduced mobility was found to be 4.10×10^{-4} m^2/V sec at 319 K and was constant over the range of E/N studied. Considering data scatter, possible errors in the determination of temperature, pressure, drift field, drift distance and time, and the possible error introduced by the hot source, the error in this mobility (one standard deviation) was found to be 3.6%. The reduced mobility of the cluster ion Li^+ (O_2) was determined from the spectra comparisons to be 2.05×10^{-4} m^2/V sec and was also independent of E/N. The error in this value (one standard deviation) is estimated to be 6.2%.

The clustering of He to Li^+ was also studied briefly at 1 Torr pressure. Only two ions were observed, Li^+ and $Li^+(He)$. We assume that the clustering process can be described by the reactions:

$$Li^+ + 2He \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Li^+(He) + He$$

The small number of cluster ions which could be counted made it impossible to deduce k_2 and k_{-2} separately, but the ratio of the counting rates for $Li^+(He)$ and Li^+ was used to deduce the equilibrium constant, $K_e = k_2/k_{-2} = 1 \times 10^{-25} m^3$ at 309 K and $E/N = 1.8 \times 10^{-20} V\ m^2$. We assume that the masses of these ions are sufficiently close to minimize problems due to differences in detection sensitivities so that this determination should be correct to within a factor of two. We did not determine the mobility of Li^+ in He. Although we know of no other direct observation of the $Li^+(He)$ cluster ion, its presence

has been inferred from low temperature mobility measurements[4] and its binding energy has been calculated to be between 0.05 and 0.07 eV.[4-8]

Lithium has been observed in the atmosphere with a peak number density of a few million atoms per m^3 at about 80 km.[9] Since a significant fraction of the lithium is expected to be positively charged,[9] it is appropriate to examine three-body loss processes of Li^+ that are revealed by our studies. Table II gives room-temperature time constants for reactions of Li^+ with N_2, O_2, and Ar at number densities appropriate to 80 km.[10] The switching reaction that could transform the initial cluster ions into $Li^+(CO_2)$ is included in the table. Since the temperature dependence of the reactions involving N_2 and those involving O_2 should be very similar, N_2 should be more important than O_2 in the three-body loss of Li^+ at 80 km. Further, the time that a $Li^+(N_2)$ cluster survives before being broken up in a collision with another molecule is long compared to the time required for it to be converted to $Li^+(CO_2)$. Thus $Li^+(N_2)$ has a much higher probability of being transformed into a more stable cluster ion than does $Li^+(O_2)$ or $Li^+(Ar)$. This result causes us to suggest that N_2 should be investigated as an important reactive species in studies of other E-region ionic constituents.

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[4] R. J. Munson and K. Hoselitz, Proc. Roy. Soc. A 172, 43 (1939).

[5] E. A. Mason and H. W. Schamp, Jr., Ann. Phys. (New York) 4, 233 (1958)

[6] A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. (London) A 259, 411 (1958).

[7] R. E. Olson, F. T. Smith, and C. R. Mueller, Phys. Rev. A1, 27 (1970).

[8] G. W. Catlow, M. R. C. McDowell, J. J. Kaufman, L. M. Sachs, and E. S. Chang, J. Phys. B 3, 823 (1970).

[9] H. M. Sullivan and D. M. Hunten, Can. J. Phys. 42, 937 (1964).

[10] COSPAR International Reference Atmosphere 1972 (Akademie-Verlag, Berlin, 1972) Part 1, p. 19.

Reference	Reaction	Rate Coefficient	Time Constant
2	$Li^+ + N_2 + N_2 \rightarrow Li^+(N_2) + N_2$	2.0×10^{-42} m^6/sec	4.1 sec
2	$Li^+(N_2) + N_2 \rightarrow Li^+ + N_2 + N_2$	7.0×10^{-21} m^3/sec	.36 sec
this work	$Li^+ + O_2 + O_2 \rightarrow Li^+(O_2) + O_2$	1.1×10^{-42} m^6/sec	28. sec
this work	$Li^+(O_2) + O_2 \rightarrow Li^+ + O_2 + O_2$	3.5×10^{-19} m^3/sec	7.2×10^{-3} sec
1	$Li^+ + Ar + Ar \rightarrow Li^+(Ar) + Ar$	1.8×10^{-43} m^6/sec	3.8×10^{3} sec
1	$Li^+(Ar) + Ar \rightarrow Li^+ + Ar + Ar$	2.0×10^{-19} m^3/sec	$12. \times 10^{-3}$ sec
estimate	$Li^+(M) + CO_2 \rightarrow Li^+(CO_2) + M$	1.0×10^{-15} m^3/sec	8.4×10^{-3} sec

TABLE II. ROOM-TEMPERATURE RATE COEFFICIENTS AND TIME CONSTANTS FOR THE CLUSTERING OF ATMOSPHERIC GASES TO Li^+ AT PRESSURES APPROPRIATE TO 80 KM. THE SYMBOL M REFERS TO N_2, O_2, or Ar.

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3. I. R. Gatland, "Ion Swarm Analysis," Technical Report of the Georgia Institute of Technology, June 1972. See also I. R. Gatland, Case Studies in Atomic Physics 4, 369 (1974).
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5. E. A. Mason and H. W. Schamp, Jr., Ann. Phys. (New York) 4, 233 (1958)
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